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Final Report

VL-2481-4-O

RAPID LINEAR PYROLYSIS OF
COMPOSITE SOLID PROPELLANT INGREDIENTS

by

D. R. Simon

R. F. McAlevy III

Distribution of this report is provided in the interest of
information exchange. Responsibility for the contents
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June 1968

Prepared for

National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23365

Under Contract

NAS1-7059

Vitro**LABORATORIES**

DIVISION OF VITRO CORPORATION OF AMERICA

200 Pleasant Valley Way, West Orange, N. J.



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TABLE OF CONTENTS

	<u>Page</u>
PROGRAM SUMMARY	1
FACILITIES DEVELOPMENT	2
Fluid Transpiration Arc	2
Radiation Arc	2
SUBSURFACE TEMPERATURE PROFILES PRODUCED BY LINEAR PYROLYSIS	6
SURFACE TEMPERATURE MEASUREMENT DURING LINEAR PYROLYSIS	8
Fine Thermocouple Measurement	8
Surface I. R. Emittance Measurement	8
Embedded Thin Carbon Film I. R. Thermopile	11
SURFACE REGRESSION RATE AND CONVECTIVE SURFACE HEAT FLUX MEASUREMENTS	13
General Discussion of Convective Surface Heat Flux to a Material Undergoing Surface Pyrolysis	13
Possibility of Kinetics Interpretation of Surface Regression Rate	14
Surface Regression Rates at High Levels of Convective Surface Heat Flux	14
Interpretation of Data in the $r - \dot{q}_{cal}$ Plane	17
REFERENCES	21

PROGRAM SUMMARY

The rapid linear pyrolysis of three model solid propellant fuel ingredients has been produced by intense levels of surface heat flux as a first step in providing the information necessary for clarification of combustion processes encountered in actual motor operation. An argon, fluid-transpiration-arc jet was employed at power input levels up to 80 kW to provide a means of convective heating of the test samples, and an arc-image radiation furnace was adapted to provide a source of radiant loading. It has been possible to provide convective heat flux as measured by a water-cooled calorimeter up to $850 \text{ cal cm}^{-2} \text{ sec}^{-1}$. At approximately $1000 \text{ cal cm}^{-2} \text{ sec}^{-1}$ the calorimeter was destroyed by this intense heating and calibration could not be made. The regression rates of polymethylmethacrylate (PMM), polystyrene (PS), and polyformaldehyde (PF) specimens produced by exposure to intense convective heating have been obtained as a function of calorimetrically measured heat flux.

Embedded, fine bead (15μ) thermocouples have been used to obtain the temperature profiles within PMM samples at various regression rates. At low regression rates (0.5 mm sec^{-1} and below) the indicated surface temperature corresponded to that measured by others.^(2,9) However, it was discovered that as the surface regression rate increased above this level the embedded thermocouple increasingly misrepresented the surface temperature. An infrared surface emission technique employed to measure surface temperature failed in a similar manner. In both cases this was due to the fact that the depth of material heated (which varies inversely with heating rate) grew small compared to the characteristic dimension over which the temperature measurement was made.

A carbon film I. R. thermopile, with a characteristic thickness of approximately 10^{-5} cm is proposed to accomplish the measurement. Fundamental interpretation of regression rate data on the basis of surface kinetics must await application of this new technique to measurement of surface temperature.

For all three thermoplastics tested, the dependence of surface regression rate on calorimetrically-measured surface heat flux becomes less with increasing heat flux. This was expected due to the "shielding" produced by the increasing vapor flux from the surface. Once the influence of this shielding can be properly taken into account, the data can be interpreted on the basis of surface energetics. This interpretation was one of the objectives of the program, however, more sophisticated experiments must be performed before it can become an accomplishment.

FACILITIES DEVELOPMENT

Fluid Transpiration Arc

An arc jet apparatus was developed to produce high levels of convective heating and arranged so as to permit incorporation of an automatic sample feed mechanism. The feed rate is variable from 0.01 mm sec^{-1} to almost 100 mm sec^{-1} . Nozzle geometries were prepared to allow both 1.9 cm dia. and 1.12 cm dia. samples to be exposed at arc jet input power levels up to 80 kW. The sample holder was fitted with a water-cooled shroud to protect the sides of the specimen from indirect heating. A photograph of arc jet impinging on a sample taken through a 700 nm interference filter is shown as Figure 1. The water-cooled shroud through which the sample fits is on the left. Convective heat fluxes up to approximately $1000 \text{ cal cm}^{-2} \text{ sec}^{-1}$ were obtained.

Radiation Arc

The modified fluid transpiration arc (FTA) has been employed as the source of radiant energy in the arc-imaging radiation furnace developed during the subject program. Delivered heat flux levels in excess of the proposed $300 \text{ cal cm}^{-2} \text{ sec}^{-1}$ were obtained. The system consists of a reflecting doublet (an opposed paraboloidal pair) which is designed to work at 1:1 magnification. An auxiliary aspherical lens is used to fill the central aperture in the primary collector mirror.

Each mirror is approximately 24" in diameter and has a 9-11/16" focal length. The complete unit, including the FTA source and collecting optics, is housed in a pressure vessel which provides an operating environment of pure argon. The radiation reaches the external test sample through an inverted quartz dome as shown in Figure 2.

A cold-wall calorimeter has been developed for calibration of the arc-imaging furnace and is shown in Figure 3. It consists of a water-cooled copper block surrounding a 6.25 cm^2 surface area made of razor blades stacked side by side. The edges of the blades, oxidized and ground to a 70° enclosed angle, make an effective black absorber for the incident radiation. The power input to the surface is then measured at equilibrium by using conventional temperature rise and flow rate measurements of the water coolant.

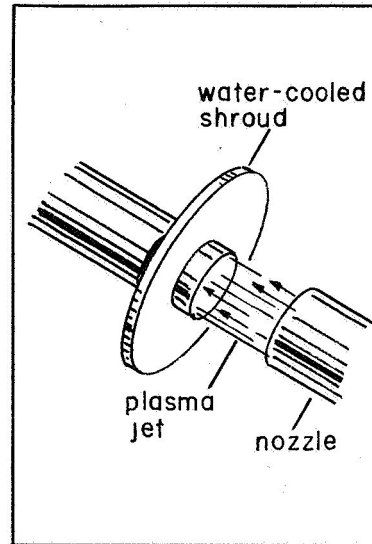
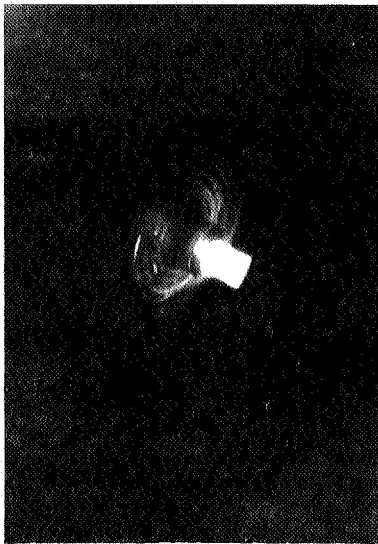
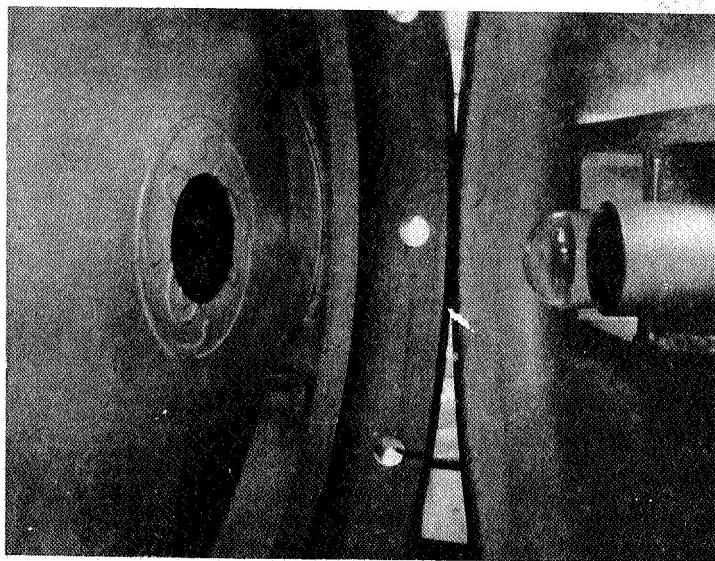
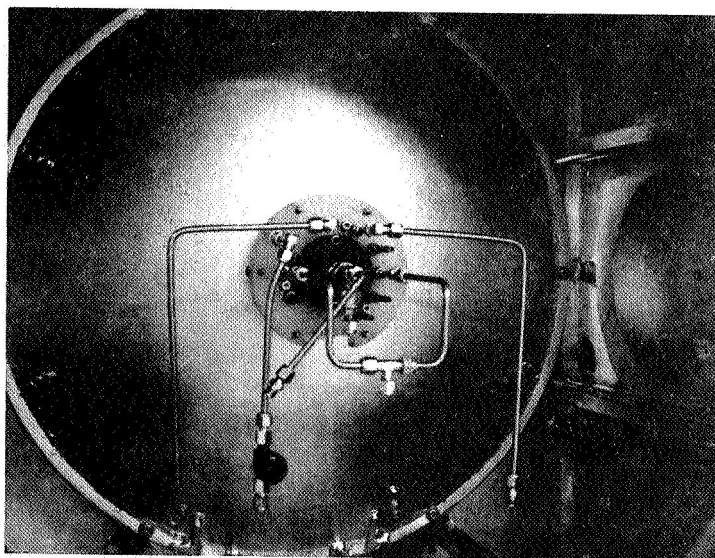


Figure 1

Arc-Jet Convective Heating of Composite Propellant Ingredient



INSERTION TUBE - #1 MIRROR



ARC SOURCE - #2 MIRROR

Figure 2

Imaging Furnace Using FTA Source

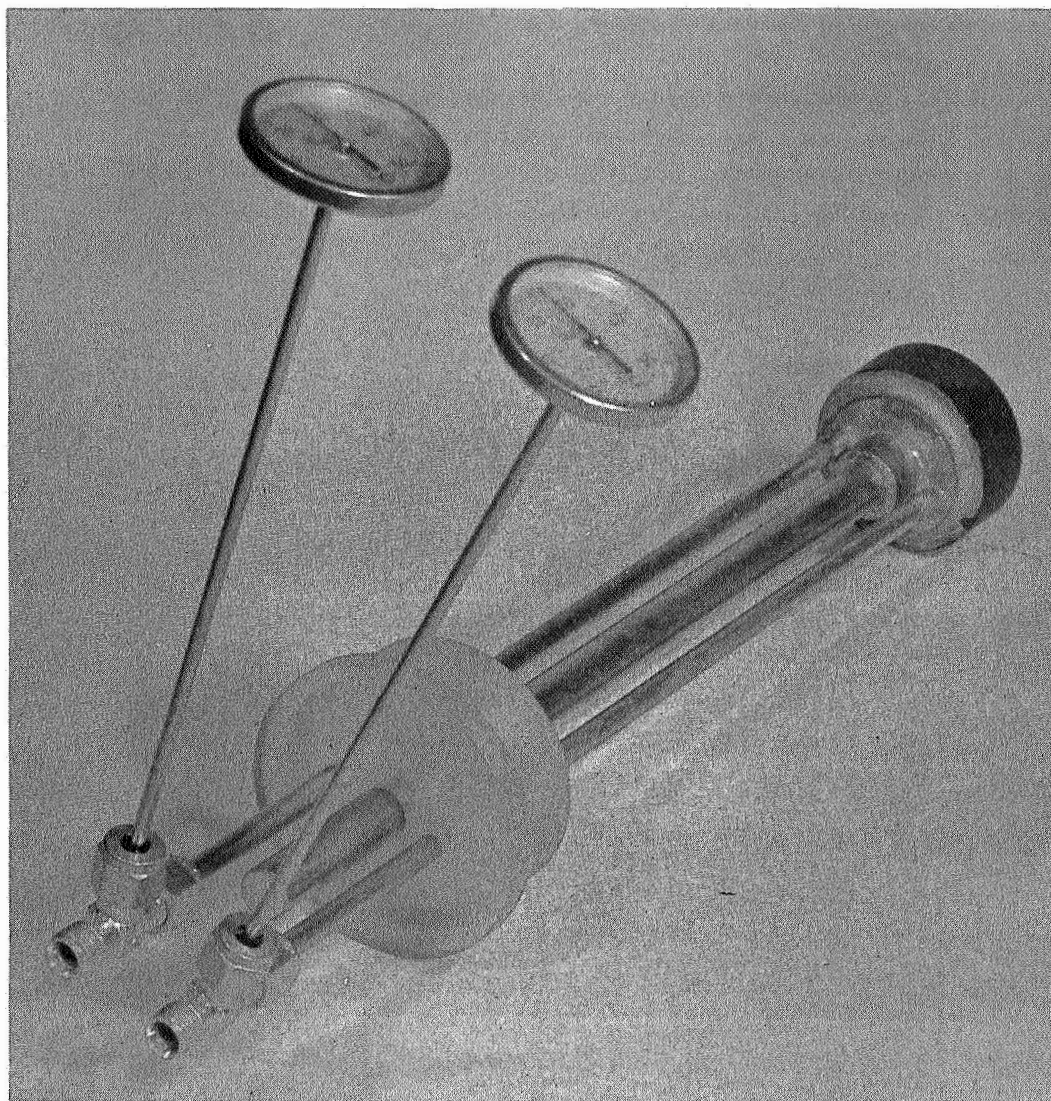


Figure 3

Cold-Wall, Optically-Black, Surface Calorimeter for
Calibration of Arc-Image Furnace

SUBSURFACE TEMPERATURE PROFILES PRODUCED BY LINEAR PYROLYSIS

The process of linear pyrolysis results in rather steep temperature profiles beneath the regressing surface. Assuming the surface regression rate is constant and that the specimen is effectively a semi-infinite, inert solid with constant properties, the subsurface temperature profile may, according to Rosenthal (Ref. 1), be represented as

$$\frac{T(x) - T_0}{T_s - T_0} = e^{-\frac{r}{\alpha} X}$$

where:

X is the distance beneath the surface.

T(x) is the temperature at position X beneath the surface.

T₀ is the temperature far beneath the surface.

T_s is the surface temperature.

α is the thermal diffusivity of the solid, assumed constant.

r is the surface linear regression rate.

Figure 4 depicts this equation. It can be seen immediately that approximately 63% (or $\frac{1}{e}$ th) of the total temperature fall from T_s to T₀ takes place in a depth beneath the surface equal to $\frac{\alpha}{r}$.

Employing a recently measured value of α for PMM, approximately $5 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$, a regression of 1 mm sec⁻¹ results in a "thermal layer" of $5 \times 10^{-3} \text{ cm}$ or 50 μ, while a regression rate of 10 mm sec⁻¹ in that of 5 μ.

As the smallest available thermocouple has a bead of 15 μ, it subtends a temperature difference of about 20% of the total - and therefore results in considerable error in measurement of T_s - at regression rates of 1 mm sec⁻¹. At 10 mm sec⁻¹ only about 1/3 of the thermocouple is immersed in the "thermal layer" as the forward edge of the bead breaks out of the surface, while 2/3 remains in contact with material still at T₀ - thus, the surface temperature indicated will be lower than T_s by hundreds of degrees.

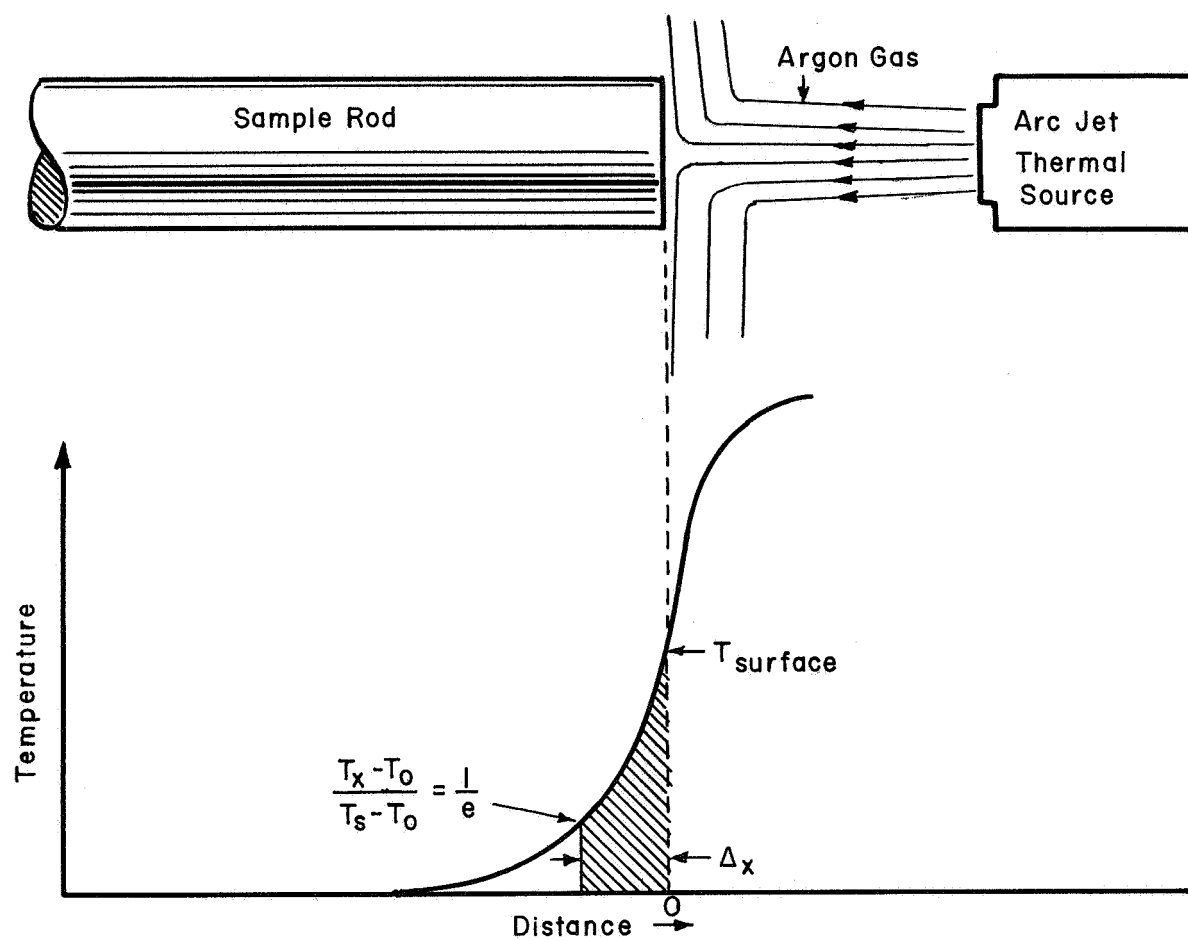


Figure 4

Subsurface temperature profile

SURFACE TEMPERATURE MEASUREMENT DURING LINEAR PYROLYSIS

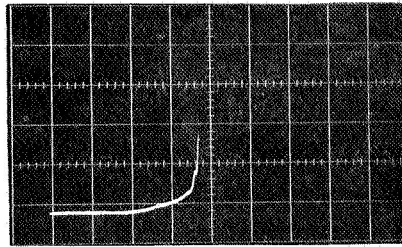
Fine Thermocouple Measurement

Fine thermocouples were mounted in samples of composite propellant ingredients and the output signal histories displayed on an oscilloscope and photographed. Figure 5 displays two such traces obtained with PMM samples at surface regression rates of approximately 0.4 mm sec^{-1} and 1.5 mm sec^{-1} . The characteristics at the lower rate correspond to those obtained by others (Ref. 2) for this material during combustion-driven surface regression rates approaching 0.4 mm sec^{-1} . That is, in both cases values of $T_s \approx 560^\circ\text{C}$ were obtained. However, in light of the discussion in Section 3.1, it is apparent that a meaningful value of T_s cannot be obtained in this way from the data obtained at a surface regression rate of 1.5 mm sec^{-1} . In fact, by blindly assuming that true levels of T_s could be obtained in this way, and not considering the potential for error discussed above, Russian workers mistakenly reported that (in ammonium perchlorate) T_s decreased with increasing r . (See discussion in Ref. 3).

Surface I. R. Emittance Measurement

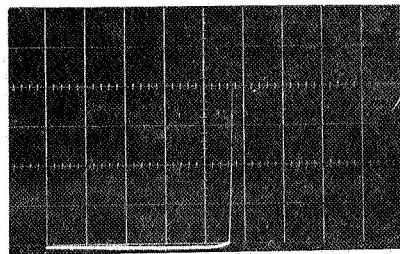
The thermal radiation from the surface of the sample was measured in an attempt to deduce the surface temperature, T_s . To apply this technique properly, it is necessary to select wavelengths where the surface radiation is not absorbed or enhanced by the mantle of vapor emerging from the surface (Ref. 4). A Beckman DK-1 recording spectrophotometer with a lead sulfide detector was employed for this work. The visible and IR spectra emitted by regressing PMM, PS, and PF surfaces, as well as the argon arc jet spectra were recorded out to 3.1μ . At regression rates of 0.4 mm sec^{-1} , several emittance peaks were observed; however, comparison with published spectra suggests these peaks were due to vapor phase emission.

To obtain meaningful values of T_s from IR radiometry, it is necessary that the hot surface layer be "optically thick." Application of Kirchoff's Law indicates that this is most likely to occur in a spectral region for which the transmittance is at a minimum. Room temperature measurements (Ref. 5) show such a minima in PMM to exist at 2.8μ . Assuming that the emissivity is not a function of temperature and applying Beer's and Kirchoff's Laws we obtain a curve of the calculated emissivity versus thickness as shown in Figure 6. The radiance of the sample in a 20 nm band centered at 2.8μ was computed from the predicted temperature profile and emissivity; the effect of radiation scattering and a possible variation of emission coefficient with temperature were neglected. The temperature profile which corresponds to



PMM subsurface temperature history obtained
at a surface regression rate of 0.4 mm sec^{-1}

time scale	5 sec cm^{-1}
amplitude	$\approx 280^\circ\text{C cm}^{-1}$



PMM subsurface temperature history obtained
at a surface regression rate of approximately
 1.5 mm sec^{-1}

time scale	0.2 sec cm^{-1}
amplitude	$\approx 600^\circ\text{C cm}^{-1}$

Figure 5

Temperature Histories Obtained as Regressing Surface Overruns
Thermocouple Bead Embedded in PMM Specimens

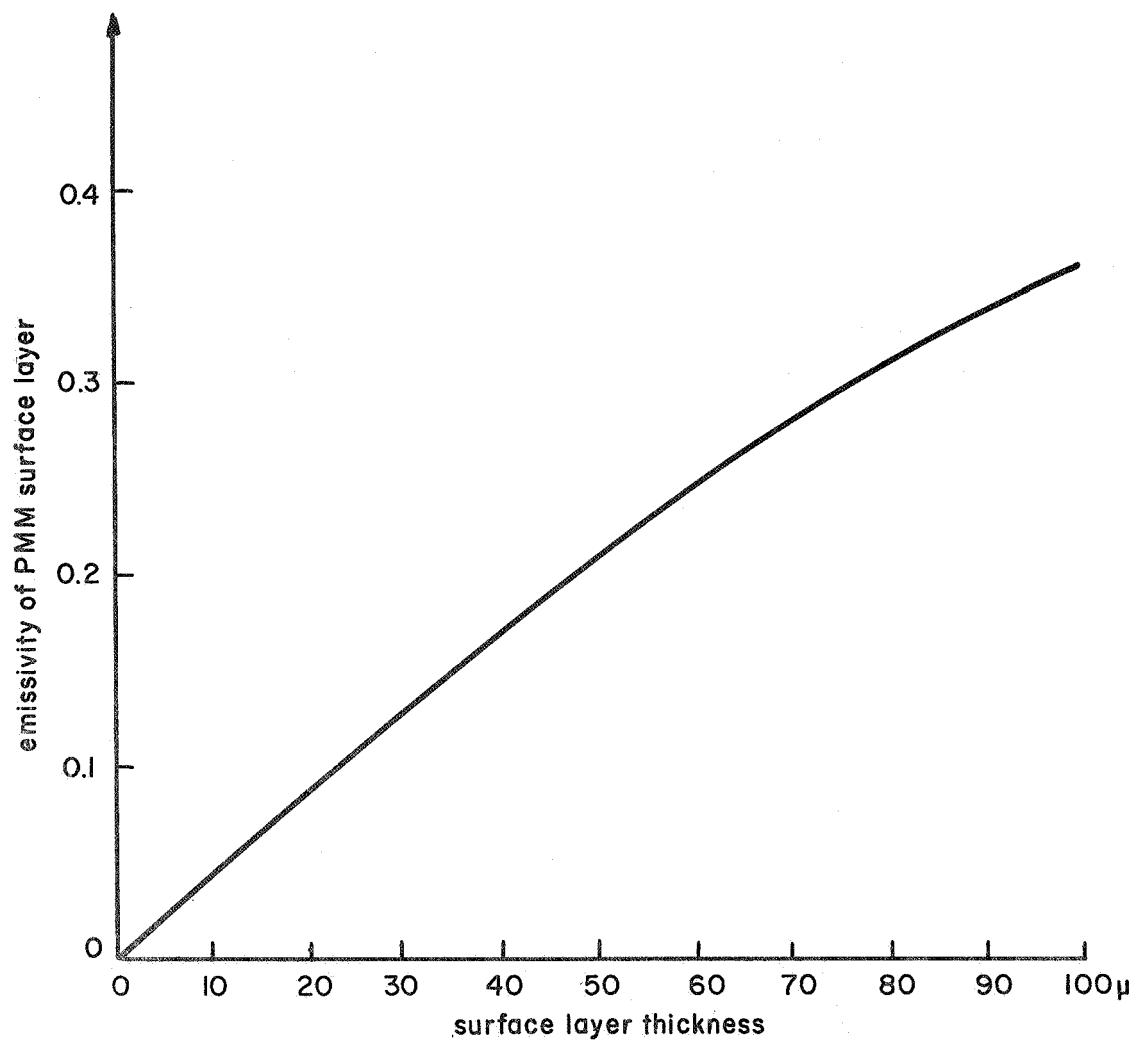


Figure 6

Calculated emissivity of surface layer
at 2.8μ .

a surface temperature of 800° K, and a regression rate of 0.4 mm sec^{-1} would emit only $1.6 \times 10^{-6} \text{ watts mm}^{-2} \text{ ster.}^{-1}$ at the surface.

This level of radiance corresponds to a black surface of 575° K, obviously a completely misleading result. Our spectrophotometer cannot detect the radiation from a black surface cooler than 700° K. The observed lack of detectable radiation from the PMM sample surface is consistent with a very steep temperature gradient as indicated by the thermocouple data.

Embedded Thin Carbon Film I. R. Thermopile

Following discovery that the techniques discussed above could not be employed to measure T_s at high values of r , a new approach was investigated. This new departure was started during the last few weeks of the subject contract year and there are no data to report. However, the technique will be outlined here. The principal reason for being optimistic about it is that the sensing element can be made on a scale that is small compared to the 5μ "thermal layer" characteristic of $r \approx 10 \text{ mm sec}^{-1}$ so that it holds the potential of measuring T_s values at high r . In fact, it is the only means for obtaining this data that is known to the authors. The approach is similar to an optical technique developed by Kantrowitz (Ref. 6). Our attempt to employ the technique involved preparation of a 3μ carbon film and mounting it in a PMM specimen, 10 mm from the surface to be heated. The general experimental arrangement to be used in the measurement of the carbon temperature is blocked out in Figure 7. The Barnes thermopile used as an I. R. sensor is interchangeable with a lead sulfide detector of higher sensitivity. The filter has an 80 nm bandwidth centered at 2.28μ , the wavelength at which the PMM sample is transparent. [An optical system (not shown in the figure) will be employed to focus on a very small area of the carbon film in order to eliminate the effects of surface regression irregularities and hence obtain the desired spatial resolution.]

This technique has sufficient sensitivity and time resolution to permit good measurements of the complete temperature profile. This type of radiometer film has been made as thin as $10^{-2} \mu$ with an aluminum face layer to reflect any radiant loading. Vitro Laboratories has submitted to NASA a proposal to exploit this technique in linear pyrolysis measurements (Ref. 8).

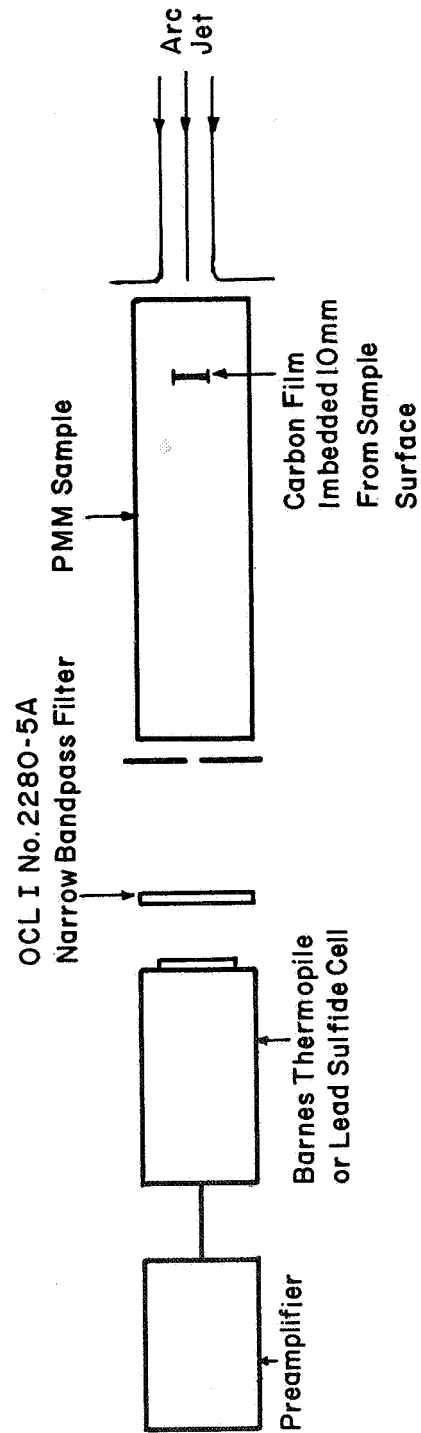


Figure 7

Schematic of thin carbon film technique
for temperature measurement.
(Focusing optics not shown.)

SURFACE REGRESSION RATE AND CONVECTIVE SURFACE HEAT FLUX MEASUREMENTS

General Discussion of Convective Surface Heat Flux to a Material Undergoing Surface Pyrolysis

The heat flowing into the surface of a material undergoing surface pyrolysis, assuming that radiation losses from the surface and internal radiation transfer are negligible, can be thought of as the sum of : (1) that required to heat the material from its initial temperature far from the surface, T_o , to the surface temperature, T_s , and (2) that required to break the chemical bonds of the material and render it to the condition of vapors leaving the surface Δh_s , that is,

$$\dot{m} [C_p (T_s - T_o) + \Delta h_s]$$

The energy flux that reaches the regressing surface is equal to that which a calorimeter would measure, \dot{q}_{cal} , minus that which is "blown" away by the vapors leaving the surface, \dot{q}_{blow} .

In the steady-state, the linearized heat balance at the regressing surface can be written as:

$$\dot{m} [C_p (T_s - T_o) + \Delta h_s] = \dot{q}_{cal} - \dot{q}_{blow}$$

The term of major interest to combustion theorists that appears in this equation is Δh_s , the same term that appears in the description of surface heat "source" or "sink" in propellant burning rate theories. However, the term \dot{q}_{blow} grows to be greater than 1/2 of \dot{q}_{cal} at the high r conditions of interest in the subject program (Ref. 8), as indicated by the calculation on pg. 3 of Ref. 2, and it involves aerodynamic factors that are sufficiently complex to preclude theoretical description within the scope of the present program. Consequently, it was decided to present regression rate and heat flux data as correlations of \dot{m} vs \dot{q}_{cal} , and thus permit the reader to select the values of \dot{q}_{blow} he deems most appropriate in order to obtain Δh_s . The reader is reminded that $C_p (T_s - T_o)$ is generally quite small compared to Δh_s and, therefore, $T_s - T_o \approx 550^\circ \text{C}$ can be employed for calculation purposes as a first approximation (Ref. 9).

Possibility of Kinetics Interpretation of Surface Regression Rate

Note that while imprecise knowledge of T_s introduces only a small error in the interpretation of surface linear pyrolysis on the basis of energetics, it makes impossible the interpretation on the basis of surface kinetics, which are a singularly sensitive function of surface temperature, that is, $\dot{m} = f(T_s)$, as discussed in Ref. (10). Such interpretation must await, therefore, the proposed T_s measurements by the carbon film technique discussed in the previous section on "Surface I. R. Emittance Measurement." An interpretation in terms of surface kinetics is impossible for the regression rates of interest from the T_s data obtained by previous techniques (see sections on "Fine Thermocouple Measurement" and "Surface I. R. Emittance Measurement").

Surface Regression Rates at High Levels of Convective Surface Heat Flux

Experiments were carried out to measure the regression rates of PMM, PS, and PF as a function of surface heat flux at exposure conditions that produced measured values of \dot{q}_{cal} up to $850 \text{ cal cm}^{-2} \text{ sec}^{-1}$. The initial data was taken at conditions producing \dot{q}_{cal} of $20 \text{ cal cm}^{-2} \text{ sec}^{-1}$. Photographs of the sample surfaces taken after each run indicated that a change in the degradation process is occurring as the flux changes from $20 \text{ cal cm}^{-2} \text{ sec}^{-1}$ to $250 \text{ cal cm}^{-2} \text{ sec}^{-1}$. Figure 8a is a typical boiled and pitted surface that was characteristic of PMM at the lower levels of \dot{q}_{cal} . Figures 8b and 8c show the progression to a smooth polished surface as the thermal loading is raised and the regression rate increases. The rate limiting factor in PMM at low thermal loadings is apparently a polymer degradation process in which the sample passes through a viscous liquid phase of some appreciable depth, and the monomer diffuses to the boiling surface. As the regression rate increases the depth of the reaction region decreases and vaporization occurs at or extremely close to the exposed surface, resulting in a smooth polished appearance. Russian workers (Ref. 11) observed the same effect during linear pyrolysis produced by pressing PMM against an electrically heated plate.

The test specimens used at the low regression rates were 1.90 cm in diameter (2.8 cm^2). The nozzle on the FTA-jet was changed for the higher heat loading experiments and the test sample diameter was reduced to 1.12 cm ($.98 \text{ cm}^2$). The data was obtained by subjecting the samples to thermal loads up to $850 \text{ cal cm}^{-2} \text{ sec}^{-1}$ only when the specimen surface remained flat during the entire test duration. The flatness of the surface depended largely on alignment with the jet axis of symmetry and the extension length from the water-cooled shroud protecting the bulk of the sample. In some cases it was necessary to coat the cylindrical surface with a zirconium-base cement in order to maintain a flat regressing surface. Figure 9 shows two of the samples after exposure



Figure 8a

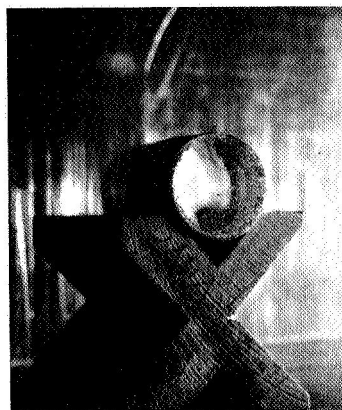


Figure 8b

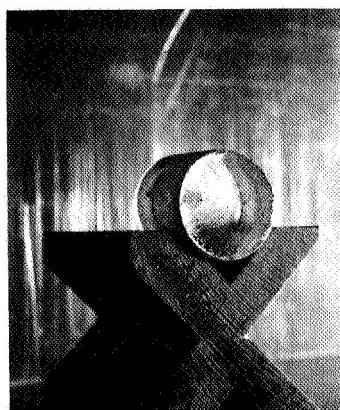


Figure 8c

Effect of Convective Surface Heat Flux Level on Pyrolyzing
PMM Surface Characteristics

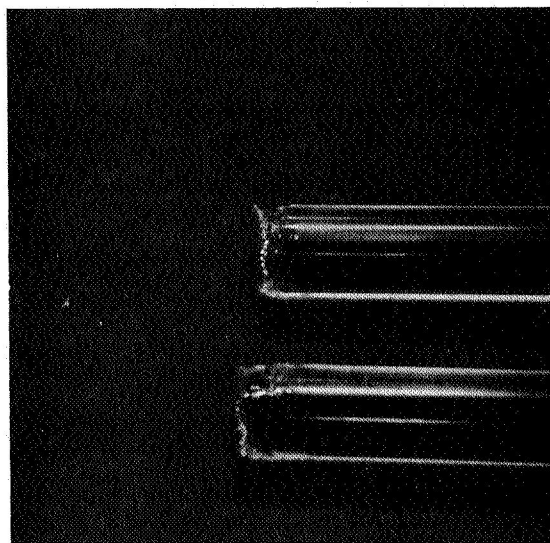


Figure 9

Two PMM Specimens Following
Exposure to Conditions that Produced $\dot{q}_{cal} = 850 \text{ cal cm}^{-2} \text{ sec}^{-1}$

corresponding to $\dot{q}_{cal} = 850 \text{ cal cm}^{-2} \text{ sec}^{-1}$ which resulted in regression rates of approximately 3 mm sec^{-1} . The data obtained from the above tests are shown in Figures 10-12. Measurements of \dot{q}_{cal} at operating conditions believed to produce levels approaching $1000 \text{ cal cm}^{-2} \text{ sec}^{-1}$ were attempted; however, the water-cooled, tungsten-faced calorimeter exploded at these levels and some design modification will be required before such large loadings can be measured.

The regression rate data displayed as Figure 10 clearly shows two slopes - at low values of r the slope is approximately $1.5 \text{ k cal gm}^{-1}$ and at high values of r the slope is approximately $4.5 \text{ k cal gm}^{-1}$.

Interpretation of Data in the $r - \dot{q}_{cal}$ Plane

As discussed in the section entitled "General Discussion of Convective Surface Heat Flux to a Material Undergoing Surface Pyrolysis," a means of assessing $\dot{q}_{b\text{low}}$, among other factors, must be at hand before the subject data can be employed to extract values for Δh_s . Nevertheless, it is possible to obtain the values of $\frac{\Delta \dot{q}_{cal}}{\Delta \dot{m}}$ or $\frac{\Delta \dot{q}_{cal}}{\Delta r}$ from Figures 10, 11 and 12. Such values correspond to the so-called "effective heat of ablation" employed in the ablative protection literature (Ref. 12) and since it reflects a complex mix of aerodynamic factors (through $\dot{q}_{b\text{low}}$) and physical factors (through Δh_s , C_p , etc.), it can have no fundamental meaning. But it is interesting to note that the values between $1.4 \text{ k cal gm}^{-1}$ and $1.6 \text{ k cal gm}^{-1}$ obtained from Figure 10 at low values of r is approximately equal to the energy required to depolymerize (Ref. 13).

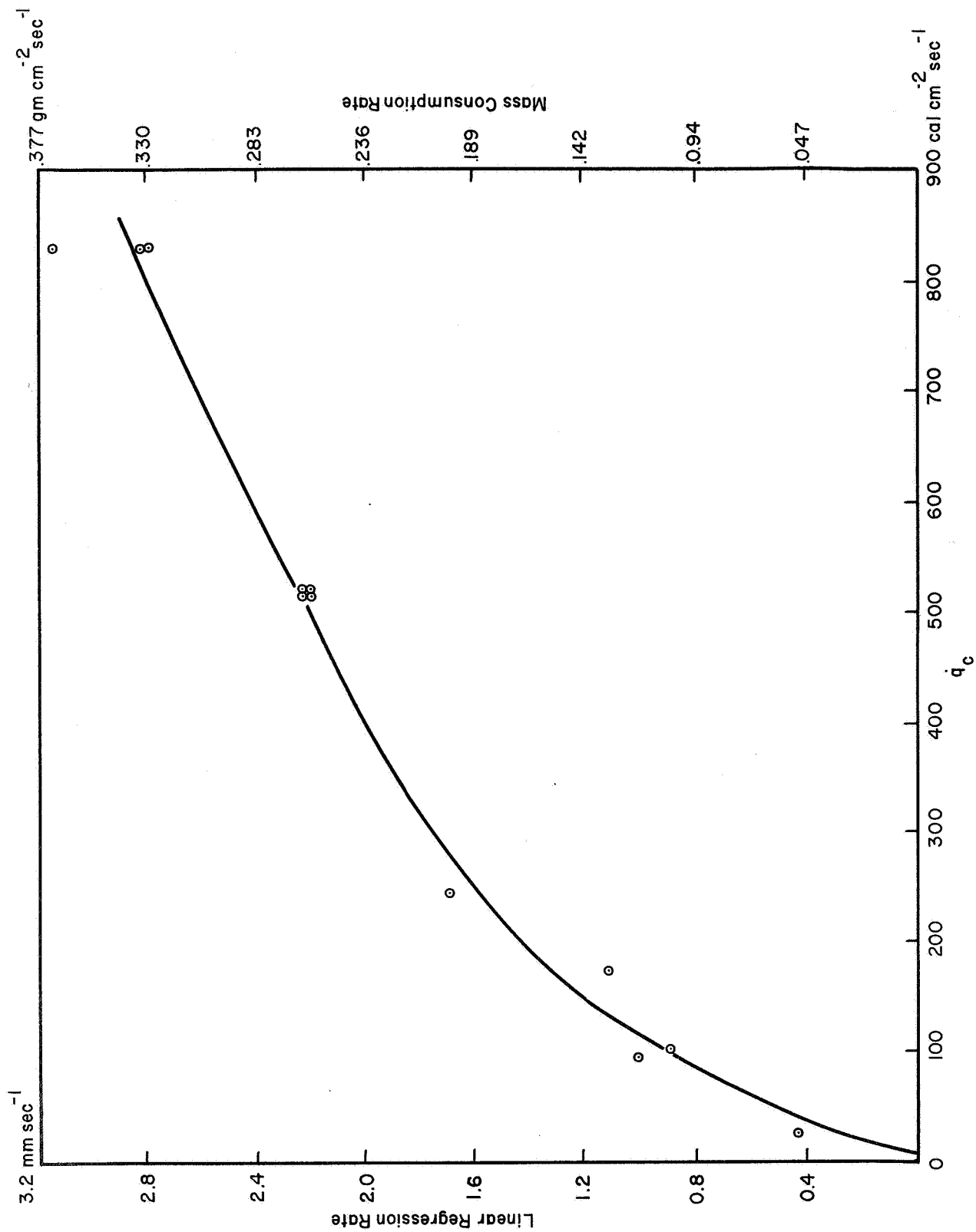


Figure 10
r and \dot{m} vs \dot{q}_{cal} for PMM

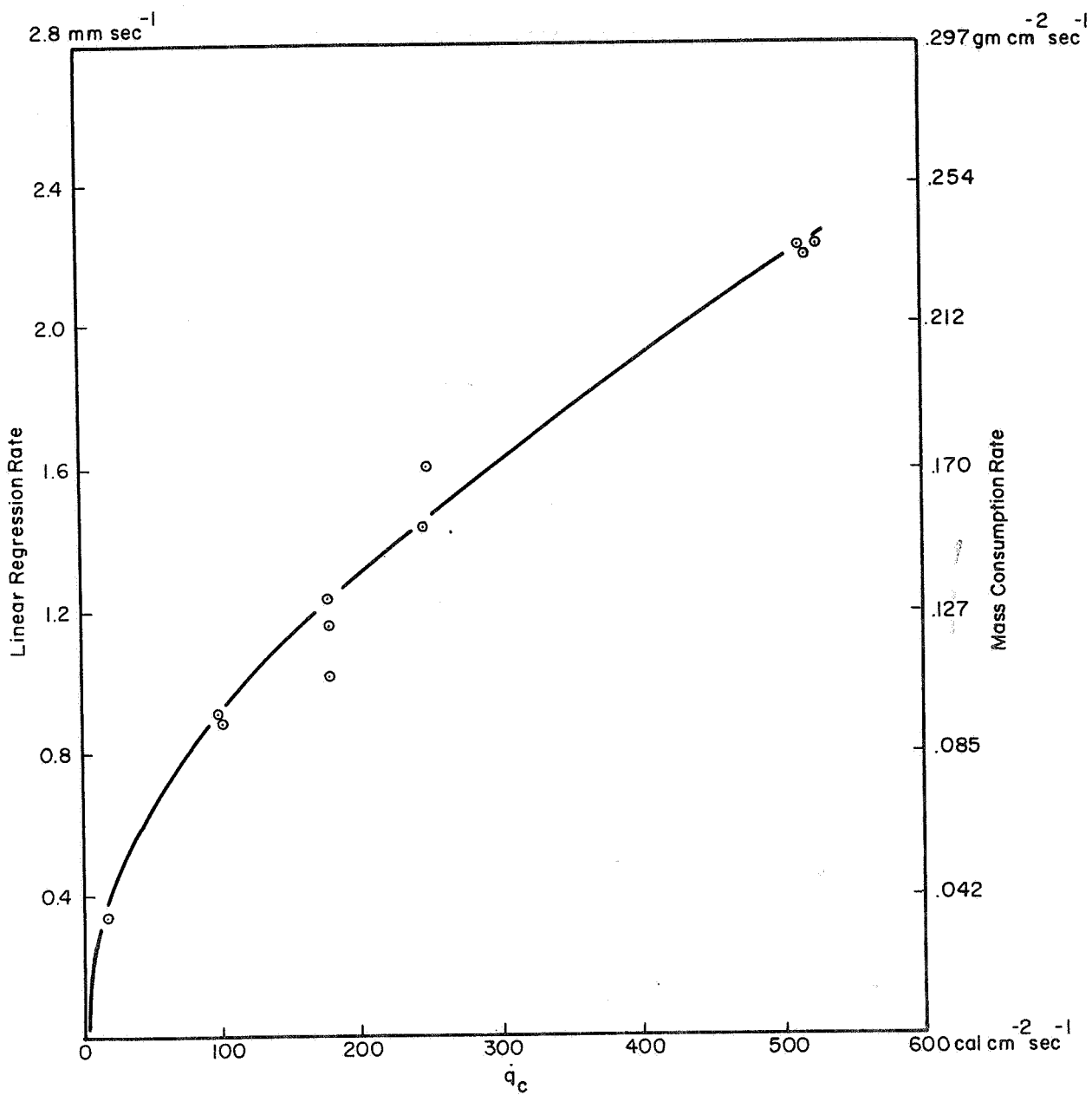


Figure 11
 r and \dot{m} vs \dot{q}_{cal} for PS

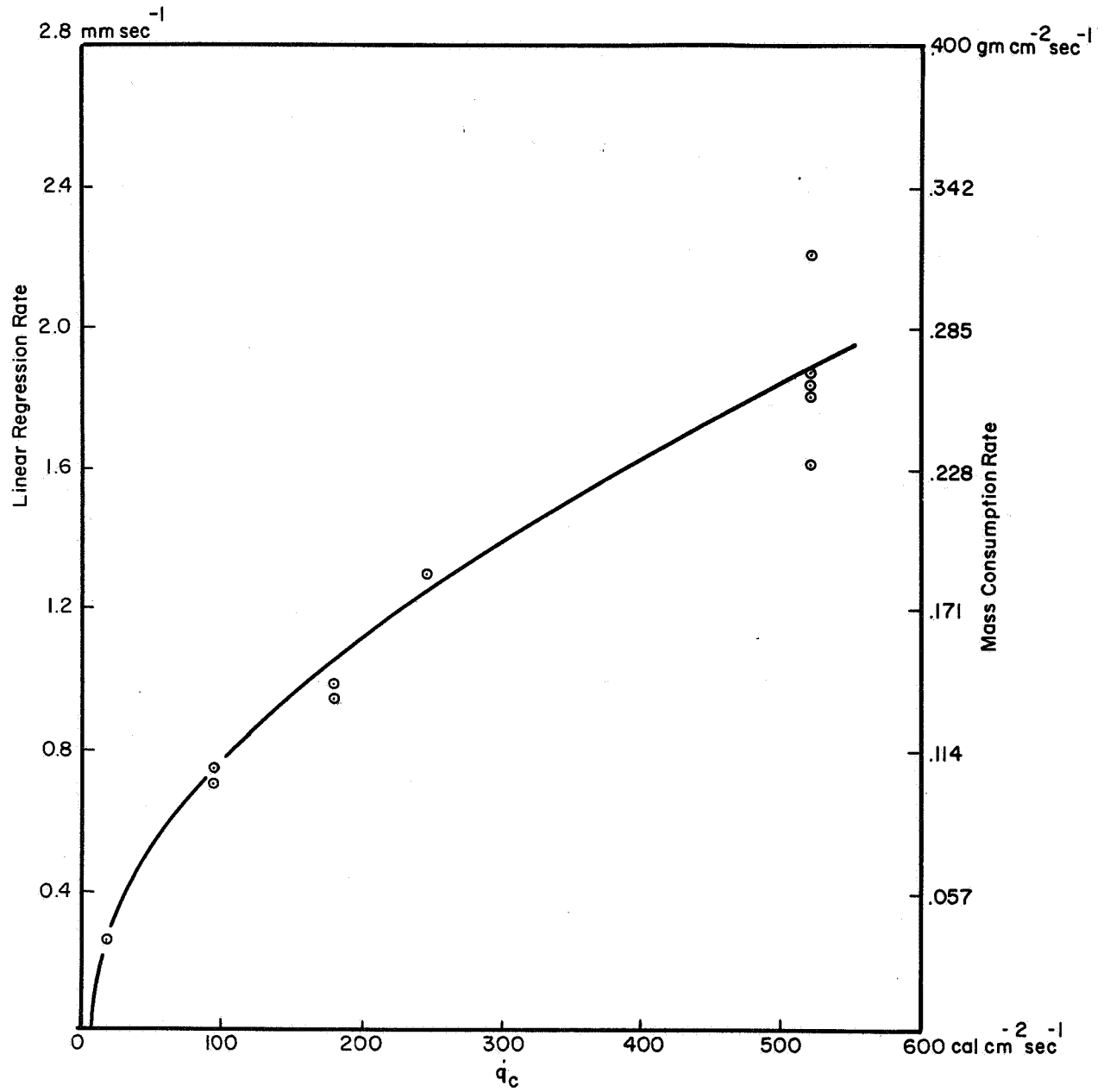


Figure 12

r and \dot{m} vs \dot{q}_{cal} for PF

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